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COMPOSITION FOR THE OXIDATION DYEING OF KERATIN FIBRES, CONTAINING A LACCASE, AND DYEING PROCESS USING THIS COMPOSITION

The invention relates to a composition for the oxidation dyeing of keratin fibres, and in particular of human keratin fibres such as the hair, comprising, in a medium which is suitable for dyeing, at least one heterocyclic oxidation dye and at least 10 one laccase-type enzyme, as well as to the dyeing process using this composition.

It is known practice to dye keratin fibres, and in particular human hair, with dye compositions containing one or more oxidation dye precursors, in particular ortho- or para-phenylenediamines, ortho- or para-aminophenols, and heterocyclic bases, which are generally known as oxidation bases. These oxidation dyes (oxidation bases) are colourless or weakly coloured compounds which, when combined with oxidizing 20 products, can give rise to coloured compounds and dyes by a process of oxidative condensation.

It is also known that the shades obtained with these oxidation bases can be varied by combining them with couplers or coloration modifiers, the latter 25 being chosen in particular from aromatic meta-diamines, meta-aminophenols, meta-diphenols and certain heterocyclic compounds.

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The variety of molecules used as oxidation bases and couplers allows a wide range of colours to be obtained.

The so-called "permanent" coloration obtained

5 by means of these oxidation dyes should moreover
satisfy a certain number of requirements. Thus, it
should have no toxicological drawbacks, it should allow
shades to be obtained in the desired intensity and it
should have good staying power with respect to external

10 agents (light, bad weather, washing, permanent-waving,
perspiration or rubbing).

The dyes should also allow grey hair to be covered and, finally, they should be as unselective as possible, i.e. they should allow only the smallest possible differences in coloration to be obtained along the same keratin fibre, which may indeed be differently sensitized (i.e. damaged) between its tip and its root.

The oxidation dyeing of keratin fibres is generally carried out in alkaline medium, in the presence of hydrogen peroxide. However, the use of alkaline media in the presence of hydrogen peroxide can have the drawback of resulting in substantial degradation of the fibres, as well as a decolorization of the keratin fibres, which is not always desirable.

The oxidation dyeing of keratin fibres can also be carried out using oxidizing systems other than hydrogen peroxide, such as enzymatic systems. Thus, it has already been proposed in US patent 3 251 742 and

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patent applications FR-A-2 112 549, FR-A-2 694 018, EP-A-0 504 005, WO 95/07988, WO 95/33836, WO 95/33837, WO 96/00290, WO 97/19998 and WO 97/19999, to dye keratin fibres with compositions comprising at least one oxidation dye, or at least one melanin precursor, in combination with laccase-type enzymes, the said compositions being placed in contact with atmospheric oxygen. Although these dye formulations are used under conditions which do not result in the degradation of keratin fibres comparable to that generated by dyes used in the presence of hydrogen peroxide, they lead to colorations that are still insufficient both in terms of the homogeneity of the colour distributed along the fibre (unison) and in terms of the chromaticity (luminosity) and dyeing power.

The Applicant has now discovered that it is possible to obtain novel dyes that are capable of giving more intense colorations without generating any significant degradation of keratin fibres, and that are relatively unselective and stand up well to the various attacking factors to which the fibres may be subjected, by combining at least one suitably selected heterocyclic oxidation dye (oxidation base and/or coupler) and at least one laccase-type enzyme.

This discovery forms the basis of the present invention.

A first subject of the invention is thus a ready-to-use composition for the oxidation dyeing of

keratin fibres, and in particular of human keratin fibres such as the hair, characterized in that it comprises, in a medium which is suitable for dyeing,

- at least one oxidation dye chosen from heterocyclic
- 5 oxidation bases and heterocyclic couplers, and
 - at least one laccase-type enzyme,

the said composition being free of heterocyclic coupler chosen from indole, indoline, monocyclic pyridine and phenazine compounds and free of heterocyclic oxidation

10 base chosen from 4,5-diamino-6-hydroxypyrimidine and

3,4-diaminohydroxypyrazole.

The ready-to-use dye composition in accordance with the invention leads to intense, chromatic colorations. The colorations obtained with the ready-to-use dye composition in accordance with the invention moreover show little selectivity and excellent properties of resistance both with respect to atmospheric agents such as light and bad weather and with respect to perspiration and the various treatments to which hair may be subjected (washing, permanent-waving).

A subject of the invention is also a process for the oxidation dyeing of keratin fibres using this ready-to-use dye composition.

The laccase(s) used in the ready-to-use dye composition in accordance with the invention can be chosen in particular from laccases of plant origin, of animal origin, of fungal origin (yeasts, moulds or

fungi) or of bacterial origin, it being possible for the organisms of origin to be monocellular or multicellular. The laccase(s) used in the ready-to-use dye composition in accordance with the invention can also be obtained by biotechnology.

Among the laccases of plant origin which can be used according to the invention, mention may be made of the laccases produced by plants which carry out chlorophyll synthesis, such as those mentioned in patent application FR-A-2 694 018.

Mention may be made in particular of the laccases present in extracts of Anacardiacea plants such as, for example, extracts/of Magnifera indica, of Schinus molle or of Pleiogynium timoriense; in extracts of Podocarpacea plants, of Rosmarinus off., of Solanum tuberosum, of Iris sp., of Coffea sp., of Daucus carrota, of Vinca minor, of Persea americana, of Catharanthus roseus, of Musa sp., of Malus pumila, of Gingko biloba, of Monotropa hypopithys (Indian pipe), of Aesculus sp., of Acer pseudoplatanus, of Prunus persica and of Pistacia palaestina.

Among the laccases of fungal origin, optionally obtained by biotechnology, which can be used according to the invention, mention may be made of the laccase(s) obtained from Polyporus versicolor, from Rhizoctonia praticola and from Rhus vernicifera as described, for example, in patent applications FR-A-2 112 549 and EP-A-504 005; the laccases described in

patent applications WO 95/07988, WO 95/33836, WO 95/33837, WO 96/00290, WO 97/19998 and WO 97/19999, the content of which forms an integral part of the present description, such as, for example, the laccase(s) obtained from Scytalidium, from Polyporus pinsitus, from Myceliophthora thermophila, from Rhizoctonia solani, from Pyricularia oryzae, and variants thereof. Mention may also be made of the laccase(s) obtained from Trametes versicolor, from Fomes fomentarius, from Chaetomium thermophile, from Neurospora crassa, from Colorius versicolor, from Botrytis cinerea, from Rigidoporus lignosus, from Phellinus noxius, from Pleurotus ostreatus, from Aspergillus nidulans, from Podospora anserina, from Agaricus bisporus, from Ganoderma lucidum, from Glomerella cingulata, from 15 Lactarius piperatus, from Russula delica, from Heterobasidion annosum, from Thelephora terrestris, from Cladosporium cladosporioides, from Cerrena unicolor, from Coriolus hirsutus, from Ceriporiopsis subvermispora, from Coprinus cinereus, from Panaeolus 20 papilionaceus, from Panaeolus sphinctrinus, from Schizophyllum commune, from Dichomitius squalens, and from variants thereof.

Laccases of fungal origin, optionally

obtained by biotechnology, will more preferably be
chosen.

The enzymatic activity of the laccases used in accordance with the invention and having

syringaldazine among their substrates can be defined by the oxidation of syringaldazine under aerobic conditions. One Lacu unit corresponds to the amount of enzyme which catalyses the conversion of 1 mmol of syringaldazine per minute at a pH of 5.5 and at a temperature of 30°C. One U unit corresponds to the amount of enzyme which produces an absorbance delta of 0.001 per minute at a wavelength of 530 nm, using syringaldazine as substrate, at 30°C and at a pH of 6.5. 10 The enzymatic activity of the laccases used according to the invention can also be defined by the oxidation of para-phenylenediamine. One ulac unit corresponds to the amount of enzyme which produces an absorbance delta of 0.001 per minute at a wavelength of 496.5 nm, using para-phenylenediamine as substrate (64 mM), at 30°C and 15

According to the invention, the enzymatic activity is preferably determined in ulac units.

at a pH of 5.

Among the heterocyclic oxidation bases which

20 can be used in the ready-to-use dye composition

according to the invention, mention may be made in

particular of pyrimidine derivatives and pyrazole

derivatives, and the addition salts thereof with an

acid.

Among the pyrimidine derivatives which may be mentioned more particularly are the compounds described, for example, in German patent DE 2 359 399 or Japanese patents JP 88-169 571 and JP 91-333 495,

such as 2,4,5,6-tetraaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine, and the addition salts thereof with an acid and pyrazolo-pyrimidine derivatives such as pyrazolo[1,5-a]pyrimidine-3,7-diamine,

- 5 2-methylpyrazolo[1,5-a]pyrimidine-3,7-diamine,
 2,5-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine,
 pyrazolo[1,5-a]pyrimidine-3,5-diamine,
 2,7-dimethylpyrazolo[1,5-a]pyrimidine-3,5-diamine,
 3-aminopyrazolo[1,5-a]pyrimidin-7-ol, 3-amino-5-
- methylpyrazolo[1,5-a]pyrimidin-7-ol,
 3-aminopyrazolo[1,5-a]pyrimidin-5-ol, 2-(3aminopyrazolo[1,5-a]pyrimidin-7-ylamino)ethanol,
 3-amino-7-β-hydroxyethylamino-5-methylpyrazolo[1,5-a]pyrimidine, 2-(7-aminopyrazolo[1,5-a]pyrimidin-
- 3-ylamino)ethanol, 2-[(3-aminopyrazolo[1,5-a]pyrimidin-7-yl)-(2-hydroxyethyl)amino]ethanol, 2-[(7-amino-pyrazolo[1,5-a]pyrimidin-3-yl)-(2-hydroxyethyl)amino]-ethanol, 5,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine, 2,6-dimethylpyrazolo[1,5-a]pyrimidine-
- 3,7-diamine and 2,5,N7,N7-tetramethylpyrazolo-[1,5-a]pyrimidine-3,7-diamine, and the addition salts thereof and the tautomeric forms thereof, when a tautomeric equilibrium exists.

Among the pyrazole derivatives which may be
mentioned more particularly are the compounds described
in patents or patent applications DE 3 843 892,
DE 4 133 957, DE 4 234 886, WO 94/08969, WO 94/08970,
DE 4 234 887, FR 2 733 749, FR 2 735 685, such as

4,5-diaminopyrazole, 4,5-diamino-1-methylpyrazole,
1-benzyl-4,5-diaminopyrazole, 3,4-diaminopyrazole,
1-benzyl-4,5-diamino-3-methylpyrazole, 4-amino-1,3dimethyl-5-hydrazinopyrazole, 4,5-diamino-3-methyl-15 phenylpyrazole, 4,5-diamino-1-tert-butyl-3methylpyrazole, 4,5-diamino-3-tert-butyl-1-methylpyrazole, 4,5-diamino-1-ethyl-3-methylpyrazole,
4,5-diamino-1-ethyl-3-(4'-methoxyphenyl)pyrazole,
4,5-diamino-1-ethyl-3-hydroxymethylpyrazole,
10 4,5-diamino-3-hydroxymethyl-1-methylpyrazole,
4,5-diamino-3-hydroxymethyl-1-isopropylpyrazole and
4,5-diamino-3-methyl-1-isopropylpyrazole, and the

addition salts thereof with an/acid.

Among the heterocyclic couplers which can be

15 used in the ready-to-use dye composition in accordance
with the invention, mention may be made in particular
of benzimidazole derivatives, benzomorpholine
derivatives, sesamol derivatives, pyrazoloazole
derivatives, pyrroloazole derivatives, imidazoloazole

20 derivatives, pyrazolopyrimidine derivatives,
pyrazoline-3,5-dione derivatives, pyrrolo[3,2-d]oxazoline derivatives, pyrazolo[3,4-d]thiazole
derivatives, thiazoloazole S-oxide derivatives and
thiazoloazole S,S-dioxide derivatives, and the addition
25 salts thereof with an acid.

Among the benzimidazole derivatives which can be used as heterocyclic couplers in the dye composition in accordance with the invention, mention may be made

more particularly of the compounds of formula (I) below, and the addition salts thereof with an acid:

$$R_{3}$$

$$N$$

$$R_{4}$$

$$R_{1}$$

$$R_{2}$$

$$R_{1}$$

$$R_{2}$$

in which:

5 R_1 represents a hydrogen atom or a C_1 - C_4 alkyl radical, R_2 represents a hydrogen atom or a C_1 - C_4 alkyl or phenyl radical,

R₃ represents a hydroxyl, amino or methoxy radical,

 R_4 represents a hydrogen atom or a hydroxyl, methoxy or

10 C_1 - C_4 alkyl radical;

with the proviso that:

- when $\ensuremath{R_3}$ denotes an amino radical, then it occupies position 4,
- when R_3 occupies position 4, then R_4 occupies position
- 15 7,
 - when R_3 occupies position 5, then R_4 occupies position 6.

Among the benzimidazole derivatives of formula (I) above which may be mentioned more

20 particularly are 4-hydroxybenzimidazole,
4-aminobenzimidazole, 4-hydroxy-7-methylbenzimidazole,
4-hydroxy-2-methylbenzimidazole, 1-butyl-4-hydroxy-benzimidazole, 4-amino-2-methylbenzimidazole,
5,6-dihydroxybenzimidazole, 5-hydroxy-6-methoxy-

benzimidazole, 4,7-dihydroxybenzimidazole,

4,7-dihydroxy-1-methylbenzimidazole,

4,7-dimethoxybenzimidazole, 5,6-dihydroxy-1-methyl-benzimidazole, 5,6-dihydroxy-2-methylbenzimidazole and 5,6-dimethoxybenzimidazole, and the addition salts thereof with an acid.

Among the benzomorpholine derivatives which can be used as heterocyclic couplers in the ready-to-use dye composition in accordance with the invention,

10 mention may be made more particularly of the compounds of formula (II) below, and the addition salts thereof with an acid:

$$Z = \begin{pmatrix} 0 \\ N \\ R_5 \end{pmatrix}$$
 (II)

in which:

15 R_5 and R_6 , which may be identical or different, represent a hydrogen atom or a C_1 - C_4 alkyl radical, Z represents a hydroxyl or amino radical.

Among the benzomorpholine derivatives of formula (II) above which may be mentioned more particularly are 6-hydroxy-1,4-benzomorpholine, N-methyl-6-hydroxy-1,4-benzomorpholine and 6-amino-1,4-benzomorpholine, and the addition salts thereof with an acid.

Among the sesamol derivatives which can be used as heterocyclic couplers in the ready-to-use dye composition, mention may be made more particularly of the compounds of formula (III) below, and the addition salts thereof with an acid:

$$R_7$$
 R_8
(III)

in which:

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- R_7 denotes a hydroxyl, amino, (C_1-C_4) alkylamino, monohydroxy (C_1-C_4) alkylamino or polyhydroxy (C_2-C_4) alkylamino radical,
- R_8 denotes a hydrogen or halogen atom or a C_1 - C_4 alkoxy radical.

Among the sesamol derivatives of formula (III) above which may be mentioned more particularly are 2-bromo-4,5-methylenedioxyphenol, 2-methoxy-4,5-methylenedioxyaniline and 2-(β -hydroxyethyl)amino-4,5-methylenedioxybenzene, and the addition salts thereof with an acid.

Among the pyrazoloazole derivatives which can

20 be used as heterocyclic couplers in the ready-to-use
dye composition in accordance with the invention,
mention may be made more particularly of the compounds
described in the following patents and patent
applications: FR 2 075 583, EP-A-119 860, EP-A-285 274,

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EP-A-244 160, EP-A-578 248, GB 1 458 377, US 3 227 554, US 3 419 391, US 3 061 432, US 4 500 630, US 3 725 067, US 3 926 631, UA 5 457 210, JP 84/99437, JP 83/42045, JP 84/162548, JP 84/171956, JP 85/33552, JP 85/43659, JP 85/172982, JP 85/190779 as well as in the following publications: Chem. Ber. 32, 797 (1899), Chem. Ber. 89, 2550, (1956), J. Chem. Soc. Perkin trans 1, 2047, (1977), J. Prakt. Chem., 320, 533, (1978); the teachings of which form an integral part of the present patent application.

Pyrazoloazole derivatives which may be mentioned most particularly are:

- 2-methylpyrazolo[1,5-b]-1,2,4-triazole,
- 2-ethylpyrazolo[1,5-b]-1,2,4-triazole,
- 15 2-isopropylpyrazolo[1,5-b]-1,2,4-triazole,
 - 2-phenylpyrazolo[1,5-b]-1,2,4-triazole,
 - 2,6-dimethylpyrazolo[1,5-b]-1,2,4-triazole,
 - 7-chloro-2,6-dimethylpyrazolo[1,5-b]-1,2,4-triazole,
 - 3,6-dimethylpyrazolo[3,2-c]-1,2,4-triazole,
- 20 6-phenyl-3-methylthiopyrazolo[3,2-c]-1,2,4-triazole,
 - 6-aminopyrazolo[1,5-a]benzimidazole,

and the addition salts thereof with an acid.

Among the pyrroloazole derivatives which can be used as heterocyclic couplers in the ready-to-use dye composition in accordance with the invention, mention may be made more particularly of the compounds described in the following patent applications and patents: US 5 256 526, EP-A-557 851, EP-A-578 248,

EP-A-518 238, EP-A-456 226, EP-A-488 909, EP-A-488 248, and in the following publications:

- D.R. Liljegren Ber. 1964, 3436;
- E.J. Browne, J.C.S., 1962, 5149;
- 5 P. Magnus, J.A.C.S., 1990, 112, 2465;
 - P. Magnus, J.A.C.S., 1987, 109, 2711;
 - Angew. Chem. 1960, 72, 956;
 - and Rec. Trav. Chim. 1961, 80, 1075; the teachings of which form an integral part of the present patent
- 10 application.

Pyrroloazole derivatives which may be mentioned most particularly are:

- 5-cyano-4-ethoxycarbonyl-8-methylpyrrolo[1,2-b]-
- 1,2,4-triazole,
- 15 5-cyano-8-methyl-4-phenylpyrrolo[1,2-b]-
 - 1,2,4-triazole,
 - 7-amido-6-ethoxycarbonylpyrrolo[1,2-a]benzimidazole, and the addition salts thereof with an acid.

Among the imidazoloazole derivatives which

- can be used as heterocyclic couplers in the ready-touse dye composition in accordance with the invention,
 mention may be made more particularly of the compounds
 described in the following patent applications and
 patents: US 5 441 863; JP 62-279 337; JP 06-236 011 and
- 25 JP 07-092 632, the teachings of which form an integral part of the present patent application.

Imidazoloazole derivatives which may be mentioned most particularly are:

- 7,8-dicyanoimidazolo[3,2-a]imidazole,
- 7,8-dicyano-4-methylimidazolo[3,2-a]imidazole, and the addition salts thereof with an acid.

Among the pyrazolopyrimidine derivatives

5 which can be used as heterocyclic couplers in the
ready-to-use dye composition in accordance with the
invention, mention may be made more particularly of the
compounds described in the following patent
application: EP-A-304 001, the teaching of which forms

10 an integral part of the present patent application.

Pyrazolopyrimidine derivatives which may be mentioned most particularly are:

- pyrazolo[1,5-a]pyrimidin-7-one,
- 2,5-dimethylpyrazolo[1,5-a]pyrimidin-7-one,
- 2-methyl-6-ethoxycarbonylpyrazolo[1,5-a]pyrimidin-7-one,
 - 2-methyl-5-methoxymethylpyrazolo[1,5-a]pyrimidin-7-one,
 - 2-tert-butyl-5-trifluoromethylpyrazolo[1,5-
- 20 a]pyrimidin-7-one,
 - 2,7-dimethylpyrazolo[1,5-a]pyrimidin-5-one, and the addition salts thereof with an acid.

Among the pyrazoline-3,5-dione derivatives
which can be used as heterocyclic couplers in the
ready-to-use dye composition in accordance with the
invention, mention may be made more particularly of the
compounds described in the following patent

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applications and patents: JP 07-036159, JP 07-084348 and US 4 128 425, and in the following publications:

- L. WYZGOWSKA, Acta. Pol. Pharm. 1982, 39 (1-3), 83.
- E. HANNIG, Pharmazie, 1980, <u>35</u> (4), 231
- 5 M.H. ELNAGDI, Bull. Chem. Soc. Jap., <u>46</u> (6), 1830, 1973
 - G. CARDILLO, Gazz. Chim. Ital. 1966, 96, (8-9), 973, the teachings of which form an integral part of the present patent application.
- 10 Pyrazoline-3,5-dione derivatives which may be mentioned most particularly are:
 - 1,2-diphenylpyrazoline-3,5-dione,
 - 1,2-diethylpyrazoline-3,5-dione, and the addition salts thereof with an acid.
- Among the pyrrolo[3,2-d]oxazole derivatives which can be used as heterocyclic couplers in the ready-to-use dye composition in accordance with the invention, mention may be made more particularly of the compounds described in patent application
- 20 JP 07 325 375, the teaching of which forms an integral part of the present patent application.

Among the pyrazolo[3,4-d]thiazole derivatives which can be used as heterocyclic couplers in the ready-to-use dye composition in accordance with the invention, mention may be made more particularly of compounds described in patent application JP 07 244 361 and in J. Heterocycl. Chem. 16, 13, (1979).

Among the thiazoloazole S-oxide and thiazoloazole S,S-dioxide derivatives which can be used as heterocyclic couplers in the ready-to-use dye composition in accordance with the invention, mention may be made more particularly of the compounds described in the following documents:

- JP 07 09 84 89;
- Khim. Geterotsilk. Soedin, 1967, p. 93;
- J. Prakt. Chem., 318, 1976, p. 12;
- 10 Indian J. Heterocycl. Chem. 1995, <u>5</u> (2), p. 135;
 - Acta. Pol. Pharm. 1995, <u>52</u> (5), 415;
 - Heterocycl. Commun. 1995, 1 (4), 297;
 - Arch. Pharm. (Weinheim, Ger.), 1994, 327 (12), 825.

The heterocyclic oxidation dye(s), i.e. the

- 15 heterocyclic oxidation base(s) and/or the heterocyclic coupler(s) preferably represent(s) from 0.0001% to 12% by weight approximately relative to the total weight of the ready-to-use dye composition, and even more preferably from 0.005% to 6% by weight approximately 20 relative to this weight.
 - The ready-to-use dye composition in accordance with the invention can also contain, in addition to the heterocyclic oxidation dyes defined above, at least one benzenic oxidation base and/or at least one benzenic coupler and/or at least one direct dye, in particular to modify the shades or to enrich them with glints.

Among the benzenic oxidation bases which may be additionally present in the ready-to-use dye composition in accordance with the invention, mention may be made in particular of para-phenylenediamines, bis(phenyl)alkylenediamines, ortho-phenylenediamines, para-aminophenols and ortho-aminophenols, and the addition salts thereof with an acid.

When they are used, these benzenic oxidation bases preferably represent from 0.0005% to 12% by

10 weight approximately relative to the total weight of the dye composition, and even more preferably from 0.005% to 6% by weight approximately relative to this weight.

Among the benzenic couplers which may be
additionally present in the ready-to-use dye
composition in accordance with the invention, mention
may be made in particular of meta-phenylenediamines,
meta-aminophenols and meta-diphenols, and the addition
salts thereof with an acid.

20 When they are present, these benzenic couplers preferably represent from 0.0001% to 10% by weight approximately relative to the total weight of the ready-to-use dye composition, and even more preferably from 0.005% to 5% by weight approximately 25 relative to this weight.

In general, the addition salts with an acid which can be used in the context of the dye compositions of the invention (oxidation bases and

couplers) are chosen in particular from the hydrochlorides, hydrobromides, sulphates, tartrates, lactates and acetates.

The medium which is suitable for dyeing (or support) for the ready-to-use dye composition in accordance with the invention generally consists of water or of a mixture of water and at least one organic solvent to dissolve the compounds which would not be sufficiently water-soluble.

The pH of the ready-to-use composition in accordance with the invention is chosen such that the enzymatic activity of the laccase is sufficient. It is generally between 4 and 11 approximately, and preferably between 6 and 9 approximately. It can be adjusted to the desired value by means of acidifying or basifying agents usually used in the dyeing of keratin fibres.

The ready-to-use dye composition in accordance with the invention can also contain various 20 adjuvants conventionally used in compositions for dyeing the hair, such as anionic, cationic, nonionic, amphoteric or zwitterionic surfactants or mixtures thereof, polymers, antioxidants, enzymes other than the laccases used in accordance with the invention, such 25 as, for example, peroxidases or 2-electron-oxidoreductases, penetrating agents, sequestering agents, fragrances, buffers, dispersants, film-forming

agents, preserving agents, opacifiers, thickeners and vitamins.

Needless to say, the person skilled in the art will take care to select this or these optionally additional compound(s) such that the advantageous properties intrinsically associated with the ready-to-use dye composition in accordance with the invention are not, or are not substantially, adversely affected by the addition(s) envisaged.

The ready-to-use dye composition in accordance with the invention can be in various forms, such as in the form of liquids, creams or gels, which may be pressurized, or in any other form which is suitable for dyeing keratin fibres, and in particular human hair. In this case, the heterocyclic oxidation dye(s) and optionally the additional oxidation dye(s) and the laccase-type enzyme(s) are present in the same ready-to-use composition, and consequently the said composition should be free of gaseous oxygen, so as to avoid any premature oxidation of the oxidation dye(s).

A subject of the invention is also a process for dyeing keratin fibres, and in particular human keratin fibres such as the hair, using the ready-to-use dye composition as defined above.

According to this process, at least one ready-to-use dye composition as defined above is applied to the fibres for a period which is sufficient to develop the desired coloration, after which the

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fibres are rinsed, optionally washed with shampoo, rinsed again and dried.

The time required to develop the coloration on the keratin fibres is generally between 3 minutes and 60 minutes and even more specifically between 5 minutes and 40 minutes.

According to one specific embodiment of the invention, the process includes a preliminary step consisting in separately storing, on the one hand, a composition (A) comprising, in a medium which is suitable for dyeing, at least one oxidation dye chosen from the heterocyclic oxidation bases and heterocyclic couplers as defined above, and, on the other hand, a composition (B) comprising, in a medium which is suitable for dyeing, at least one laccase-type enzyme, and then in mixing them together at the time of use, after which this mixture is applied to the keratin fibres.

Another subject of the invention is a multicompartment dyeing device or "kit" or any other multicompartment packaging system, a first compartment of
which contains composition (A) as defined above and a
second compartment of which contains composition (B) as
defined above. These devices may be equipped with a
means for applying the desired mixture to the hair,
such as the devices described in patent FR-2 586 913 in
the name of the Applicant.

The example which follows is intended to illustrate the invention without thereby limiting its scope.

DYEING EXAMPLE

The following ready-to-use dye compositions were prepared (contents in grams):

COMPOSITION	1	2
2,4,5,6-Tetraaminopyrimidine sulphate	0.65	-
(heterocyclic oxidation base)		
para-Phenylenediamine (benzenic oxidation	-	0.20
base)		
Resorcinol (benzenic coupler) /	0.30	
2-Methoxy-4,5-methylenedioxyaniline	-	0.37
monohydrochloride (heterocyclic coupler)		
Laccase obtained from Rhus vernicifera at	1.8	1.8
180 units/mg, sold by the company Sigma		
Common dye support (*)	(*)	(*)
Demineralized water qs	100 g	100 g

(*): Common dye support:

- Ethanol

20.0 g

10 - (C8-C10)alkylpolyglucoside as an aqueous solution containing 60% active material (A.M.), sold under the name Oramix CG110® by the company Seppic

4.8 g A.M.

15 - Agent for pH q.s.

pH = 6.5

Each of the ready-to-use dye compositions described above was applied to locks of natural grey hair containing 90% white hairs, for 40 minutes at a temperature of 30°C. The hair was then rinsed, washed with a standard shampoo and then dried.

The hair was dyed in the shades given in the Table below:

EXAMPLE	Shade obtained	
1	Coppery mahogany light blond	
2	light blond	

In the dye compositions described above, the laccase from Rhus vernicifera at 180 units/mg, sold by the company Sigma, can be replaced with 1.0 g of laccase from Pyricularia oryzae at 100 units/mg, sold by the company ICN.